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Subtractive methods to form pyrite and sulfide nanostructures of Fe, Co, Ni, Cu and Zn

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ABSTRACT

The low *Z* metals Fe, Co, Ni, Cu and Zn are Earth abundant, i.e. inexpensive, and their sulfides are of low toxicity. This makes them appealing candidates for materials applications requiring semiconductors or, in the case of CoS_2, a metal since they can potentially be produced in large quantities and low cost. Though of great potential little work has explored how subtractive methods can be used to form nanostructured and/or porous structures in, e.g. FeS_2, CoS_2, NiS, Cu_2S and ZnS.

The pyrite and sulfide compounds FeS_2, CoS_2, NiS, Cu_2S and ZnS represent an interesting class of materials. All are semiconductors except for CoS_2, which is metallic. FeS_2 and Cu_2S, in particular, have been flagged as potential candidates for large-scale photovoltaic deployment [1]. Iron pyrite (FeS_2) nanoparticles occur naturally and may make up as much as 10% of the dissolved iron emanating from some black smoker hydrothermal vents [2].

Hollow and/or porous particles and films have advantages over solid structures and films in many applications because they offer higher specific surface area and better permeability. They may also possess unique surface properties, particularly if they are crystalline. Therefore, they often represent better candidates for a broad range of applications in photonic crystals, drug delivery, sensors and catalysts, including photocatalysis. Porous oxides and zeolites are numerous and well studied [3]. Porous sulfides are much less commonly encountered. As an example, it is noted that mesoporous ZnS have been shown [4] to exhibit enhanced photocatalytic activity toward the reduction of eosin B.

FeS_2 is an excellent material for high-energy density lithium and sodium ion batteries [5,6]. It has already been demonstrated to enhance the performance of primary batteries compared to conventional alkaline cells. The use of iron pyrite in rechargeable batteries has been more difficult but may be facilitated by encapsulation in carbon [7]. Nanostructuring of electrodes is an effective approach to improve the capacity and kinetics of electrode materials by reducing the ion/electron diffusion distance, increasing electrode/electrolyte contact area, and better accommodating the strain associated with the lithium insertion/removal reaction [8]. In this respect the formation of FeS_2 nanowires [9] or nanocrystals [10] could be quite promising.

Iron pyrite has also attracted considerable attention in the realm of photovoltaics (PV) and photocatalysis (including water splitting to evolve H_2) because of its favorable optical properties. It has a bandgap of 0.95 eV and exhibits an optical absorption coefficient in excess of 5×10^5 cm^{-1} below 700 nm while maintaining excellent electron mobility. Bandgap optimization might also be used to enhance photocatalytic activity by control of nanocrystal size [11]. However, low photovoltage, S deficiencies and poor structural uniformity have limited PV applications. Kirkeminde et al. [12] have demonstrated that FeS_2 nanocrystals exhibit plasmonic photoelectron conversion. The localized surface plasmon resonances (LSPR) arising from this might be harnessed to increase the efficiency of bulk heterojunction (BHJ) solar cells.

Metal chalcogenides including CuS have shown promise as a replacement for Pt in dye sensitized (DSSC) or quantum dot sensitized solar cells (QDSSC) [13]. Cu_2S nanoparticles exhibit promise for use in plasmonic devices [14].

Nanoparticles are desirable in a number of biomedical applications. FeS nanoplates are magnetic and have been investigated as

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potential theranostics agents [15]. CuS nanoparticles are effective absorbers of near-infrared light. They have attracted interest as a photothermal coupling agent for cancer therapy because they are lipophilic, which translates into a high tissue affinity [16].

In addition to their magnetic properties, nickel sulfide nanoparticles have garnered attention as a toughening agent in window glass and as infrared detectors. More interesting yet are their applications in catalysis, such as hydrodenitrogenation and hydrodesulfurization reactions as well as photocatalysis [17]. NiS_2 improves the catalytic activity of MoS_2 for hydrodesulfurization by forming $NiMoS_x$.

Cobalt pyrite CoS_2 is a particularly interesting material for use in the hydrogen evolution reaction (HER). CoS_2 is catalytically active and metallic, which means that it represents an excellent candidate to replace noble metals as an electrode material. For maximum efficiency, high surface area resulting from nano- and microstructuring to produce a porous but electrically interconnected electrode is optimal. Faber et al. [18] demonstrated increased electrocatalytic activity of CoS_2 nanowire electrodes versus planar film electrodes toward polysulfide and triiodide reduction. Covering the surface of electrodes with nanowires might also improve the performance of quantum dot- and dye-sensitized solar cells. Much like FeS_2 and NiS_2, CoS_2 exhibits long-term stability in both acidic and alkaline operating environments.

However here, I would like to focus not on the exploitation of additive synthesis methods, i.e. growth, but rather on subtractive methods in which etching plays a role. The most well-developed case study in this realm is that of Si. Si is unique among materials because large single crystals of Si are readily available in incredible purity and a variety of orientations at reasonable cost. Thus, nanocrystalline porous silicon with pores ranging from the mesoporous to macroporous range can be produced easily by anodic [19], galvanic [20] or stain etching [21] as well as other means [22]. However, also silicon powder can be porosified by stain etching [23]. Because of its biocompatibility, silicon is of increasing interest for applications such as drug delivery [24] and as nanoneedles [25]. The self-limiting nature of silicon etching in fluoride solutions allows its etch chemistry to exhibit such a facile and versatile range of nanostructure formation [26].

Nanostructure formation by etching is certainly not limited to Si. A great advance in this area is represented by Masuda–Schmuki chemistry. It has long been known that anodization of metals at high biases can lead to pitting corrosion [27–29]. However, it was not until Masuda and co-workers [30–32] demonstrated the amazing ease with which self-ordered hexagonal arrays of porous alumina could be fabricated on a large scale that great interest in the high-voltage anodization of metals in acidic solutions became of general interest. Schmuki broadened the approach vastly by the introduction of fluoride into the electrolyte as well as expanding beyond aqueous solvents into viscous organic solvents. Schmuki and co-workers have now demonstrated that high-voltage anodization of polycrystalline foils can produce porous nanostructures in a variety of metals and alloys. By far the best-studied case is that of TiO_2 nanotube formation [33–35]. However, oxide nanotubes can also be formed from pure metals such as Hf, Ta, W, Nb, and Zr, as well as alloys such as TiNb, TiZr, TiAl, Ti_6Al_7Nb, Ti_6Al_4V and $Ti_{29}Nb_{13}Ta_{4.6}Zr$ [36]. Ordered porous arrays can be formed in Ta and Nb [36]. A more random porous oxide can be produced from Co, which after annealing yields Co_3O_4. V_2O_5 can be produced as ordered nanopores/nanotubes [37]. Nanotubular/nanoporous films of Fe_2O_3 can also be formed by anodization of Fe or FeSi alloys [38].

An example of the use of a subtractive method for the formation of a pyrite nanostructure is found in the work of Shi et al. [39]. They started by forming iron oxide nanotubes anodically. Sulfuration was then performed at 400 °C in the presence of 80 kPa of S vapor for 5 h to form FeS_2 nanotubes. This suggests that many of the metal oxides that form nanotubes and porous structures can be converted to sulfide nanotubes and porous sulfides. The extent of structure retention, phase purity, and conditions required to optimize these parameters remain to be discovered. The relative advantages of sulfuration with elemental S as compared to, e.g., H_2S need to be investigated.

Another subtractive technology is laser ablation. Laser ablation has been extensively used for the growth of thin films. It is well known that nanoparticles are made in the laser ablation plume [40,41]. More recently, it has been recognized that near-threshold ablation is also an effective means of surface modification. One of the most celebrated examples is the formation of black silicon [42] – extremely low reflectivity surfaces caused by the presence of laser ablation pillars. Laser ablation pillars can also be formed in numerous other materials including Ti [43], Ge [44], Ni [45], Al, Cu and stainless steel [46]. Femtosecond laser patterning of metals can produce colored films [47]. The pattern of pillars can be replicated by transference into a PDMS mold [48]. Silicon pillars are readily reshaped by anisotropic etching into extremely sharp, high-aspect ratio (>5000) needles [49] that can then be porosified [50] or transformed into crystallographically defined macropores [51].

The size range and specific shape of laser ablation pillars can be varied by the use of different laser parameters (wavelength, pulse length, number of shots, fluence, multiple-beam interference, etc.) and performing ablation in the presence of different gases [46,52,53]. Laser ablation pillars greatly increase the surface area of the substrates. The surfaces of the pillars can themselves exhibit structure from the nano- to the micro-scale. Sulfur is incorporated into the Si lattice when ablation is performed in the presence of SF_6. The associated changes in electronic structure reduce the reflectivity of the surface below that induced by the geometry of the surface alone [54]. Nonetheless, very little work has been performed on chemical modification of laser ablation pillars and their transformation into sulfides.

A different approach to subtractive nanostructure formation is the coating of a sacrificial phase with a material of interest. The sacrificial phase is then removed by etching or dissolution. For example, silica nanospheres are etched with HF and polystyrene nanospheres are dissolved by acetone or toluene. Mondal et al. [17] combined ultrasonic spray pyrolysis with a template of silica nanospheres to produce hollow, porous NiS_2 nanospheres.

This short and non-comprehensive comment is meant to highlight a few points. One is fairly well known. Pyrite and sulfide nanostructures of the Earth abundant metals Fe, Co, Ni Cu and Zn have great potential for applications in materials science. The next is that these materials are somewhat undervalued. They have yet to reach their potential because methods of producing them phase pure and in the form required have often not yet been achieved. While many methods have been applied to the formation of pyrite and sulfide nanostructures, in my opinion, subtractive methods have yet to be exploited in this area, which provides for fertile opportunities going forward.

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